Journal of Chemical Physics 2007 vol.126 N9

Molecular diffusion on a time scale between nano- and milliseconds probed by field-cycling NMR relaxometry of intermolecular dipolar interactions: Application to polymer melts

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Abstract

A formalism is presented permitting the evaluation of the relative mean-squared displacement of molecules from the intermolecular contribution to spin-lattice relaxation dispersion of dipolar coupled spins. The only condition for the applicability is the subdiffusive power law character of the time dependence of the mean-squared displacement as it is typical for the chain mode regime in polymer liquids. Using field-cycling NMR relaxometry, an effective diffusion time range from nano- to almost milliseconds can be probed. The intermolecular spin-lattice relaxation contribution can be determined with the aid of isotopic dilution, that is, mixtures of undeuterated and deuterated molecules. Experiments have been performed with melts of polyethyleneoxide and polybutadiene. The mean-squared segment displacements have been evaluated as a function of time over five decades. The data can be described by a power law. The extrapolation to the much longer time scale of ordinary field-gradient NMR diffusometry gives good coincidence with literature data. The total time range thus covers nine decades. © 2007 American Institute of Physics.

http://dx.doi.org/10.1063/1.2435357